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14. ABSTRACT Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS), which contain silicon-oxygen cores and a periphery of long chain fluorinated alkyl groups, were functionalized with methyl methacrylate (MMA) and acrylate (A) to produce F-POSS monomers (F-POSS-MMA and F-POSS-A). Structures were confirmed with multinuclear NMR (¹ H, ¹³ C, and ²⁹ Si) and found to be soluble in non-fluorinated solvents such as diethyl ether. F-POSS-MMA was found to display similar wetting properties to unmodified F-POSS with advancing (θ_{adv}) and receding (θ_{rec}) contact angle measurements of $118.2 \pm 1.0^\circ$ and $90.6 \pm 1.0^\circ$ for water, and $76.8 \pm 0.3^\circ$ and $64.8 \pm 1.0^\circ$ for hexadecane, respectively. Contact angle measurements for F-POSS-A were found to be nearly identical to F-POSS-MMA. F-POSS-MMA was subsequently used to produce F-POSS-PMMA-co-PMMA via the free radical polymerization of F-POSS-MMA and MMA. The synthesis of these monomers and their subsequent polymerizations represent the first successful synthesis of covalently bound F-POSS polymer composites.					
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FLUOROALKYL POLYHEDRAL OLIGOMERIC SILSESQUIOXANE (F-POSS) BASED MONOMERS AND POLYMERS

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Introduction

Fluorinated Polyhedral Oligomeric Silsesquioxanes (F-POSS), contain a silicon-oxygen core [SiO_{1.5}] with a periphery of long-chain fluorinated alkyl groups, were recently developed for low-surface energy materials.^{1,2} F-POSS possess one of the lowest surface energy values known ($\gamma_{sv} = 9.3$ mN/m) and have led to the creation of numerous superhydrophobic and oleophobic surfaces.^{3,4} F-POSS compounds are capable of producing superhydrophobic and superoleophobic surfaces when cast on a substrate or blended within a polymer matrix.^{3,5,6} Typically, these composites are based on the physical blending of F-POSS into a polymer matrix. To date, there has been no viable method to covalently attach F-POSS to a polymer matrix in order to improve the composite's mechanical robustness. The incorporation of covalently bound POSS moieties to polymer matrices has yielded composites with enhanced mechanical properties has only been demonstrated with non-fluorinated POSS structures.⁷⁻⁹ Herein, we report the synthesis and characterization of F-POSS monomers based on methacrylate and acrylate moieties. Methacrylate F-POSS structures were subsequently used to produce F-POSS/PMMA copolymers via free radical polymerization. These materials possess potential applications in superhydrophobic/oleophobic coatings and low-surface energy materials.

Experimental

Materials. All dichlorosilanes were purchased from Gelest and used without further purification unless otherwise noted. Compound **1** was synthesized according to previously described procedure.¹⁰ All reactions were performed under a nitrogen atmosphere unless otherwise noted.

Instrumentation. ¹H, ¹³C, ¹⁹F, and ²⁹Si NMR spectra were obtained on a Bruker 300-MHz or 400-MHz spectrometer. A heteronuclear inverse gated decoupling pulse sequence (NOE) with a 12 sec delay was used to acquire ²⁹Si NMR spectra. Contact angle measurements were taken on an optical contact angle system OCA (Dataphysic).

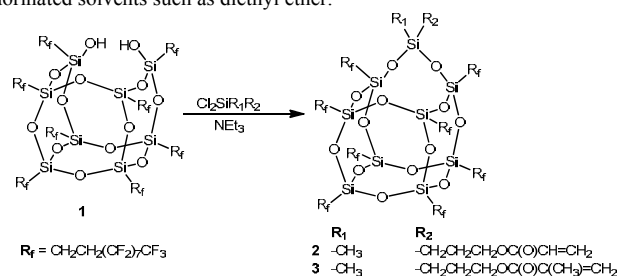
General synthesis of F-POSS monomers. A solution of **1** (4.00 g, 0.99 mmol), 3-acryloxypropylmethylchlorosilane (0.226 g, 0.99 mmol), and NEt₃ (0.200 g, 1.95 mmol) were stirred together for 12 hr. During this time a white precipitate formed. The solution was then filtered and poured into ethyl acetate, at which time, a white solid precipitated (F-POSS). This solid was removed via filtration and the filtrate was concentrated, then dissolved in diethyl ether and filtered. The filtrate was collected and cooled to 0 °C affording a white precipitate. The precipitate was collected and dried under vacuum to afford a white powder (**2**) (1.9 g, 48%). ¹H NMR (300 MHz, (CD₃CD₂)₂O, ppm) δ 6.01 (s, 1H), 5.56 (s, 1H), 4.16 (t, 2H), 2.25 (m, 16H), 1.92 (s, 3H), 1.84 (m, 2H), 1.09 (m, 16H), 0.76 (t, 2H), 0.26 (s, 3H). ²⁹Si {¹H} NMR δ -18.1, -66.08, -68.64, -69.2 (1:2:4:2). ¹⁹F NMR -82.26 (3F), -116.9 (2F), -122.6 (6F), -123.7 (2F), -124.3 (2F), -127.3 (2F).

General Polymerization of F-POSS monomers. Methyl methacrylate (MMA, 1.31 g, 13.1 mmol), **3** (0.36 g, 0.09 mmol), azobisisobutyronitrile (AIBN, 5 mg, 0.001 mmol) were dissolved in a fluorinated solvent:THF mixture (4:1). This solution was purged with nitrogen for 25 minutes to remove any oxygen and was immediately submerged in a 65 °C oil bath for 18 hrs. The resulting solution was precipitated in hexanes, filtered and dried to yield a fluffy white powder (0.93 g, 71%).

Contact angle measurements. F-POSS compounds (10 mg/mL) were dissolved in a fluorinated solvent and spun cast at a rate of 900 rpm for 30 seconds onto oxygen-plasma treated 1-inch silicon wafers. Measurements were taken in triplicate.

Results and Discussion

Synthesis of F-POSS monomers. The incompletely-condensed silsesquioxane **1** can be readily reacted with a variety of dichlorosilanes (Scheme 1). For example, the reaction of **1** with 3-acryloxypropylmethylchlorosilane in the presence of triethylamine produced compound **2** (ca. 48%). The main side product isolated during the reaction was closed-cage F-POSS. Multinuclear NMR (¹H, ²⁹Si, ¹⁹F) was used to confirm the structure of **2**. The ²⁹Si peaks were observed at resonances of -18.1, -66.08, -68.64, and -69.2, with a ratio of 1:2:4:2 (Figure 1). The resonance at -18.1 ppm was attributed to the 3-acryloxypropylmethyl functionalized Si. These compounds, **2** and **3**, possess acrylate and methacrylate functionality, making them ideal candidates for copolymerization. Interestingly, both of these compounds are soluble in non-fluorinated solvents such as diethyl ether.



Scheme 1. Synthesis of disilanol F-POSS.

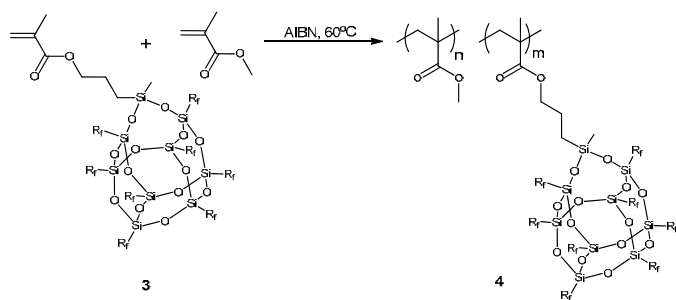
Contact angle measurements of F-POSS monomers. The wetting properties of F-POSS make it one of the lowest surface energy materials known. To demonstrate that F-POSS monomers retained their impressive wetting properties, advancing (θ_{adv}) and receding (θ_{rec}) contact angle measurements were taken with water and hexadecane (Table 1). Compared to unfunctionalized F-POSS and open-caged **1**, these modified F-POSS structures possess similar wetting properties to their predecessors. Both compounds **2** and **3** exhibited similar wetting properties towards water and hexadecane. There was an observed increase in contact angle hysteresis for compounds **2** and **3** when wetted with water. These initial observations will be explored in further detail to elucidate the impact of functionality on the wetting-properties of F-POSS.

Table 1. Contact angle measurements of F-POSS monomers

Compound	water		hexadecane	
	(θ_{adv})	(θ_{rec})	(θ_{adv})	(θ_{rec})
F-POSS*	122 ± 2	116 ± 2	80 ± 1	61 ± 3
(1)	116.8 ± 0.4	111 ± 0.6	77.4 ± 0.4	74.4 ± 0.8
(2)	118.2 ± 1.0	90.6 ± 1.0	76.8 ± 0.3	64.8 ± 1.0
(3)	117.1 ± 0.6	93.8 ± 1.5	78.1 ± 0.4	63.0 ± 1.2

*Reported values for F-POSS⁴

Synthesis of copolymers. Methyl methacrylate modified F-POSS (**3**) was copolymerized with MMA via thermally-initiated AIBN-initiated free radical polymerization to produce a PMMA-co-F-POSS copolymer (**4**) (Scheme 2). These initial polymerizations were performed at a low molar ratio of **3**:MMA (1:144) due to the large molecular weight of compound **3** (4,178 g/mol). Multinuclear NMR was used to characterize (¹H, ¹⁹F) the polymer. ¹H NMR revealed resonance signals at 0.5 – 2 ppm and 3.6 ppm which were attributed to PMMA. The resonances observed in the ¹⁹F NMR spectrum were attributed to the fluorinated chains on F-POSS (Figure 1). Currently, molecular weights of these polymers are being obtained to determine the impact of F-POSS in the polymerization of these monomers. The wetting behavior of these polymers is being investigated as well.



Scheme 2. Copolymerization of F-POSS MMA and MMA.

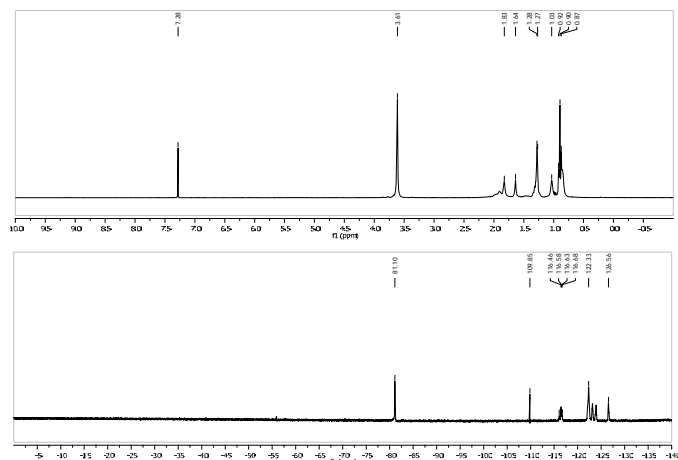


Figure 1. ^1H NMR (top) and ^{19}F NMR (bottom) of copolymer 4 taken in CDCl_3 .

Conclusions

Methacrylate and acrylate functionalized F-POSS structures were synthesized and characterized via multinuclear NMR and contact angle analysis. These compounds were found to display wetting properties similar to unmodified F-POSS. Methacrylate F-POSS was subsequently used to produce F-POSS-PMMA copolymer via free radical polymerization. These novel structures can be used in the development of new superhydrophobic and oleophobic materials.

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